

## PATENT SPECIFICATION

DRAWINGS ATTACHED

1025.694



Date of Application and filing Complete Specification: Jan. 11, 1963.

No. 1402/63.

Application made In United States of America (No. 173,872) on Feb. 19, 1962.

Complete Specification Published: April 14, 1966.

© Crown Copyright 1966.

Index at acceptance:—B2 B(4E1C1, 4E3C, 4E3D, 4E6A, 4C6C, 4A7A1, 4E7A2, 4E7AX, 4E7AY, 4E7B3, 4E7B4, 4E7BX, 4E8G, 4E9P, 4E9Q2, 4E9Q4, 4E9Q7, 4E9Q8, 4E9Q10, 4E9Q11, 4E9Q12, 4E9QX, 4E9QY); E2 E1E; C1 A(C3C4, K4, N13A, N24B, N34); C1 D(6A1B, 6A2J, 6B4); C2 C2B41; C3 R(22C5, 22C6, 22C8, 22C9, 22D1A2, 22D2AX, 22N1A, 22PX); C4 A5; E1 K17

Int. Cl.:—B 44 d // C 01 b, g, C 06 b, d, C 07 c, C 08 g, C 09 d, D 04 h

## COMPLETE SPECIFICATION

## Polymer Coating of Solid Particles

We, NORTH AMERICAN AVIATION, INC., a Corporation organised and existing under the laws of the State of Delaware, United States of America, of 1700 East Imperial Highway, El Segundo, State of California, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the manufacture of polymer-coated solid particles.

It is often necessary or desirable to employ small solid particles of material in an environment in which they would normally react prematurely, be physically attached, or subject to radiation before use in their intended final application. It has been proposed to coat these particles with a protective barrier which either completely protects the particle or which can be removed prior to the end use application. In general these coatings have been applied by precipitation of the coating material from solution or by bulk contact of the coating material with the particle to be coated. When solution precipitation is employed it is often difficult to remove all the solvent from the coating. Bulk contact has the disadvantage that the coated particles tend to agglomerate into relatively large masses. It is preferable that the coating process should produce individually coated particles with little change in size or shape.

It is therefore an object of this invention to provide a process for the preparation of solid particles having protective polymer coatings, enabling the coating to be uniform and free from inclusions of solvent.

According to the present invention there is provided a process for preparing a solid particulate material coated with a polymeric material, which process comprises mixing a solid particulate substance and a polymerizable liquid material under turbulent conditions and in the presence of an inert non-solvent liquid carrier so as to coat the solid with the polymerizable liquid and thereafter polymerizing the polymerizable liquid to a polymeric solid while maintaining turbulent conditions and thereby producing discrete solid particles coated with a solid polymeric material. Curing agents, catalysts, and other ingredients may be included with the polymerizable materials if liquid in form, or with the solid substances if solid in form or may be added as separate components.

Mixing of the solid particulate substances and polymerizable liquids in the inert carrier may be conducted in a variety of ways. The polymerizable liquid and solid particulate material may be added to the inert carrier while the carrier is maintained under constant agitation. Another embodiment of the invention comprises continuously metering portions of the particulate solids and polymerizable liquid into a flowing stream of the inert carrier. Another embodiment of this invention comprises pre-slurrying one of the components, preferably the solids, in the inert carrier, and then adding the other component while agitating the slurry. This embodiment may also be conducted in a continuous fashion by metering one component into a flowing stream of

the slurry of the other component. Still another embodiment of the invention comprises forming separate dispersions of both components and bringing streams of the dispersions together in either a batch or continuous fashion.

The polymerizable liquid may include polymer-forming, resinous and plastic materials which are initially liquids and which, upon curing by chemical means or the application of heat, or a combination of chemical means and heat application, form solid cohesive substances. Curing may be conducted at ambient or elevated temperatures depending on the particular polymer employed.

The polymerizable liquid may be monomeric or may be in a partially polymerized viscous form. The dispersion of this polymeric material when employed is therefore a dispersion of a liquid in a non-miscible and non-solvent liquid and may be in proportions such that the weight ratio of dispersed polymerizable liquid to dispersion medium is from 1:20 to 1:1. More dilute dispersions can also be employed but ordinarily are not desirable in order to minimize the handling of excessive amounts of dispersant. An example is the dispersion of a polymer of di(thioethoxy)methylene, having an average molecular weight of about 2000 and a viscosity of substantially 1000 centistokes of 20° C. in n-heptane. The dispersion is formed by agitation as with a mechanical stirrer until the composition approaches a state of emulsion. This polymer dispersion is then blended with a dispersion of a filling material such as a dispersion of solid ammonium perchlorate in n-heptane, and the polymer is cured (that is, further polymerized) while agitation is maintained.

The solid particulate material, which may be pre-dispersed, may be in a finely divided form of particle size ranging from 1 to 1000 microns in diameter. This particle size is obtained in the original preparation of the material or by grinding, pulverizing or otherwise comminuting the solid.

In order to prevent agglomeration of the coated particles, it is preferred to employ particles of substantially uniform size.

The solid particles may be pre-dispersed in the non-solvent, non-reactive vehicle, as for example, ammonium perchlorate in n-heptane, by mixing, stirring or other means of agitation. The ratio by weight of dispersed solid to dispersion medium may fall within the range of from 1:20 to 1:1. More dilute dispersions can also be used but will usually not be employed in order to avoid handling excessive amounts of diluent. The dispersion medium is one which is miscible with and may be the same as the medium employed in dispersing the polymeric substance. The dispersed solid is then blended or mixed with the other components in the presence of the inert carrier. The mixture is stirred, shaken, or otherwise agitated until a uniformly dispersed composition results. The temperature at which the dispersions and the blending are carried out is not critical. Ordinarily, these operations are carried out at ambient temperatures although temperatures of up to the boiling point of the diluent or dispersant can be used. The time required for agitation is also not critical and can vary from a few minutes to an hour or more. Following this, agitation is continued until curing is complete. The dispersed polymeric material and solid particles, upon contact, form a new dispersion which settles out of the inert carrier if agitation is not continued. After curing is complete, the supernatant dispersion medium is removed by decantation, evaporation or other means well known in the art. The solid polymer coated solid particles may then be further processed if necessary for its use in its intended purpose, such as inclusion in a rocket propellant.

While the method of this invention may be performed as a batch process, it is preferred to carry out the processes in a continuous manner which reduces the energy requirements for physical agitation to ensure thorough mixing of the polymerizable material and the solid being dispersed therein. This is accomplished by bringing separate streams of the polymerizable materials and solid dispersions together into a common stream and effecting mixing by the turbulence set up at the point at which the two streams join. One method of accomplishing this is by metering a flow of one dispersion into a stream of the other dispersion as it is conducted from the dispersion container to a receiving vessel through a pipe or other appropriate channel. Another method of mixing is by bringing two channels of the separate dispersions together and allow mixing to be effected by the turbulence set up at the point of junction of the two channels. The proportions in which the two dispersions are combined is controlled by regulating the rate of feeding of the separate components from their respective containers into the channels. Curing may also be conducted in either a batch or continuous fashion.

The invention further comprises coated particles produced by the processes

described above. Further description by way of example follows with reference to the accompanying drawing in which:

Fig. 1 illustrates a system in which two different dispersions are brought together and fed as a mixed stream into a receiving vessel. Fig. 2 illustrates a system in which the carrier and each of the components are fed into a mixing zone and the resulting mixture collected in a heated and agitated receiving vessel. Fig. 3 illustrates a system in which one component is pre-mixed in the carrier and the other component added to the slurry in a mixing zone.

In Fig. 1, a dispersion of a polymerizable material in a non-solvent and non-reactive liquid dispersion medium is contained in tank 10 and a dispersion of a solid particulate substance also in a non-solvent and non-reactive liquid dispersion medium is contained in tank 11. The two dispersion mediums are mutually miscible. The dispersion from tank 10 is fed through line 12 into line 13 in an amount which is controlled by valve 14 in line 12. Simultaneously, the dispersion from tank 11 is fed through line 15 into line 13 in an amount which is likewise controlled by valve 16. The dispersions from tanks 10 and 11 come in contact with each other at junction 17 of the lines 12 and 15. The flow rate is adjusted so that the turbulence set up at this point causes efficient mixing of the two streams so that the solid particles are coated with the polymerizable material on contact, and while dispersed in the carrier are fed through line 13 into vessel 18. The vessel 18 is equipped with agitation means such as impeller 19 to maintain the coated particles as individual discrete entities in the carrier, and heating means such as the heated jacket 20, to accomplish cure of the polymer.

In Fig. 2, tanks 21, 22 and 23 contain the dispersion medium, the polymerizable liquid and the solid, respectively. Material from these tanks is fed through conduits 24, 25 and 26 respectively into mixing zone 27. The amounts of the different materials fed into this mixing zone are controlled by valves 28, 29 and 30 or other suitable metering devices. Rates are adjusted so that the turbulence set up in the mixing zone is sufficient to cause efficient mixing of the components so that a uniform composition of solid coated with the polymerizable material empties from the mixing zone 27 dispersed in the carrier and flows into the line reactor 39 where the dispersed resin coated solid material is cured by the action of heating jacket 40 which is filled with a heated fluid 41. The individual coated particles are prevented from coagulating into a solid mass by maintaining sufficient velocity through the line reactor. After leaving the line reactor, the coated solids are removed from the carrier.

In Fig. 3, a dispersion of solid material is fed from tank 31 through line 32 into a mixing zone 33 which empties into a heated chamber 34. The polymerizable liquid is metered into the mixing zone 33 through line 35 and is blended with the dispersion of the solid, thus coating the solid. The coated solids dispersed in the carrier flow to the chamber 34 through the line 36. Chamber 34 is heated by jacket 37 and the contents are maintained under constant agitation by the impeller 38. In order to provide for a completely continuous process, a plurality of chambers such as 34 may be provided and may be filled sequentially through the line 36. Coated particles in each chamber may then be cured after the chamber is filled.

The solid particulate material employed in the process of this invention can be any organic or inorganic solid whether naturally occurring or synthetically prepared. Both polymeric and non-polymeric materials may be used. Thus, thermoplastic, thermosetting, elastomeric, polymeric plastic, non-polymeric organic and inorganic materials may be employed. These materials may be either naturally occurring, modified materials occurring in nature, or synthetically prepared, and may be employed if they are particulate solids.

Among the solid thermoplastic materials which may be employed are polymers and copolymers of mono-olefinic hydrocarbons having at least two carbon atoms per molecule. Thus, the polymers and copolymers of ethylene, propylene, various butenes, pentenes, and hexenes, as well as the halogenated counterparts of these olefins may be employed in the practice of this invention. Among the thermosetting polymeric materials which may be employed are those plastics and resins which have been cured to a solid upon the application of heat with or without a chemical curing agent. Illustrative examples of this class of material include the polyurethane resins, epoxide resins, polyester materials, and thioplasts (polysulfide polymers). In addition, elastomers, such as the natural and synthetic rubbers in particulate form may be practicably and profitably employed in the practice of this invention. The synthetic rubbers are ordinary polymers and copolymers of a diolefin as a major constituent which contain other olefin constituents and which are subject to vulcanization subsequent to polymerization.

to cross-link the polymer through any remaining carbon-to-carbon double bonds. In addition to the above, organic polymers derived from naturally occurring non-elastomeric polymeric materials may be employed in the practice of this invention.

In general, solid carbohydrate condensation-type polymers, amino-acid condensation polymers, synthetic linear condensation polymers including the polyamides and polyesters, linear addition polymers such as hydrocarbon and vinyl-type polymers, and cross-linking polymers may be employed in the process of this invention.

The carbohydrate condensation-type polymers are cellulose, cellulose nitrate, and modified nitrated cellulose compositions, cellulose acetate, cellulose acetate-butyrate, ethylcellulose, and the cellulose ethers such as methyl carboxymethyl, hydroxyethyl, cyanethyl and benzyl cellulose. In addition, such carbohydrate polymers as starch, chitin, and formaldehyde polymers may be employed.

Examples of the solid amino-acid condensation polymers are regenerated proteins such as casein and vegetable globulins. Synthetic linear condensation polymers which may be employed in the practice of this invention include the polyamides such as nylon, and polyurethane resins, polyesters such as the alkyd and fiber-forming types, polyester and polyesteramide rubbers.

Applicable solid linear addition polymers include natural and vulcanized rubbers such as gutta-percha, balata, and chicle, cyclized or isomerized rubber, rubber hydrochloride, polybutadiene rubbers including GR-S and nitrile rubber, polychloroprene and its copolymers, polysulphide rubbers, polyisobutylene and the butyl rubbers, the various polyethylenes including chlorosulphonated polyethylene rubber, polytetrafluoroethylene, polystyrene, polyvinylcarbazole and polyacenaphthylene, indene and coumarone-indene resins, polyvinyl acetate, polyvinyl alcohol, polyvinyl pyrrolidone, polyvinyl formal, polyvinyl acetal, and polyvinyl butyral, polyvinyl chloride, vinyl chloride-vinyl acetate copolymers, polyacrylonitrile, vinyl chloride-acrylonitrile copolymers, polyvinylidene chloride and its copolymers, polymethyl methacrylate and related polyacrylates, ketone aldehyde polymers and polyacrylate rubbers.

Solid cross-linking polymers applicable to the present invention include cross-linking type polyester resins, various epoxy resins, polymerized drying oils, aniline formaldehyde resins, sulphonamide-formaldehyde resins, urea-formaldehyde resins, melamine-formaldehyde resins, and the various phenol-formaldehyde condensation resins.

Furthermore, solid organic polymers containing elements other than carbon, hydrogen oxygen, and nitrogen may be employed. For example, silicon-containing polymeric materials are advantageously adapted to the practice of this invention. The silicon-containing polymers fall into two general classes; those having direct silicon-to-silicon bonds (the silanes) and those having silicon-bonded to silicon through oxygen (the siloxanes). The silicon-containing materials often have a halogen in the molecule.

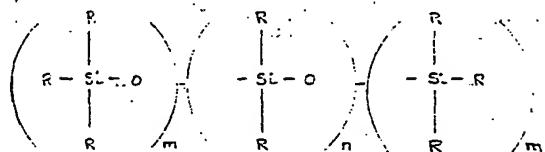
The solid particulate material employed in the process of this invention is ordinarily employed in finely divided form having a particle size ranging from 1 to 1000 microns in diameter. In many applications more than a single solid particulate material may be employed and the solid materials may vary in particle size range. These solids may be coloring agents, pigments, diluents, asbestos fibres, powdered metals, inorganic compounds such as salts, or metal oxides, or any other suitable solid particulate material. Examples of inorganic solids include pigments such as titanium dioxide, lead dioxide, ferric oxide, carbon black, metal powders such as aluminum, copper, lithium and sodium, and various inorganic salts, highly reactive inorganic materials used in propellant and explosive composition, and fertilizer components.

In addition, depending upon the intended use of the material, various other additives in minor quantities may be incorporated in the composition by initially mixing all of the ingredients in the presence of the inert carrier.

The liquid vehicles which are used as the inert carriers or dispersion mediums must be non-solvent and non-reactive with respect to the substances being mixed according to the process of this invention. The same medium may be used for both the solid materials and the polymerizable liquids or conversely different vehicles or dispersion mediums may be employed for the polymerizable liquid and each of the solid components when the components are pre-dispersed prior to mixing. It is required only that the dispersion media for the components be non-reactive to any of the substances employed and that the media be mutually miscible. Examples of dispersion media which are employed in the carrying out of the process of this invention include water, aliphatic and olefinic hydrocarbons having from 3 to 16 carbon atoms per molecule. Examples of these are propane, butane, hexane, heptane, octane, dodecane, and hexa-

decane as well as 2-octene, 1-dodecene, and 1-hexadecene. Examples of cyclic hydrocarbons are cyclohexane and methylcyclohexane. Examples of aromatic and alkyl-aromatic compounds which are employed as dispersion mediums include compounds having from 6 to 16 carbon atoms per molecule such as benzene, toluene, xylene, 2,4-diphenylbenzene, phenyldecanes, decalin, and 1-hexyldecalin. Halogen derivatives of the above hydrocarbons are also employed as dispersion mediums. Examples of these include ethylenedichloride, trichloroethylene, methylenedichloride, chlorobenzene, bromobenzene, and iodobenzene. Compounds of the "FREON" (Registered Trade Mark) series such as dichlorodifluoromethane and dichlorotetrafluoroethane, may also be employed.

The liquid lower alkyl siloxanes may also be employed as a carrier in the process of this invention. The applicable alkyl siloxane compounds have a general formula:



wherein R is a lower alkyl or hydrocarbon radical having up to 8 carbon atoms, n is an integer from 0 to 6, and m is 1 or 0 such that when m is 0, n has the value of from 3 to 5 and the compound is cyclic. Thus, siloxane liquids used in the practice of this invention are pure siloxanes or mixtures thereof and include the cyclic polysiloxanes and the straight and branch chain silane-terminated siloxanes. Therefore, the cyclic polysiloxanes having from 3 to 6 repeating siloxane groups may be employed in this invention. The preferred hydrocarbon substituent in the siloxane fluids is the methyl group.

Other possible dispersion mediums are alcohols having from 1 to 12 carbon atoms per molecule and from 1 to 3 hydroxyl groups per molecule. Examples of these are methyl alcohol, ethyl alcohol, isopropyl alcohol, benzyl alcohol, glycerine and dodecyl alcohol. Amines may also be used which have from 2 to 12 carbon atoms per molecule and from 1 to 3 nitrogen atoms per molecule. These include such compounds as ethylenediamine, diethylenetriamine, dodecylamine, pyridine and quinoline. Ethers, ketones, aldehydes and esters having from 2 to 16 carbon atoms per molecule are also used. Examples of these are ethyl ether, acetone, propionaldehyde, ethyl acetate, butyl dodecanoate, and 2-butoxyethanol. The requirement in all of these cases is that the dispersion medium not be reactive to any of the polymeric or solid components employed and also that they be non-solvent toward these components. In addition, when different dispersion media are used for the polymerizable material and the solid components, and any plasticizer which may be employed (further discussed hereinafter), it is necessary that these dispersion media be miscible one with the other. The properties of these various dispersion media with respect to miscibility and solvent power are well known to those skilled in the art and will not be discussed further. In the process of this invention, it is ordinarily preferred to employ non-aqueous carriers or dispersion media, and particularly those organic, low viscosity organic carriers which are free of reactive groups. The dispersion may be formed with the aid of heat in cases where the dispersion medium is very viscous at ambient temperature or the plasticizer has a high melting point. The methods of preparing the dispersion themselves are well known and do not merit further discussion here.

The polymerizable liquid materials which provide the coating of the solid particles according to the process of this invention are, in general, thermosetting materials which exist in the liquid state in either monomeric or partially polymerized form and which are either self curing to a solid or cure to a solid under the influence of a catalyst or in combination with one or more copolymerizable liquid pre-polymers or monomers. Some of the many classes of thermosetting applicable to this invention include the phenolic resins, ethoxylin or epoxy resins, polyurethane resins, acrylate resins, vinyl polymers containing reactive groups, the thioplasts, diene polymers terminated with reactive groups and methylol acrylamide polymers. These thermosetting liquid materials are so well known in the art as to require no further detail in this specification.

Plasticizers and diluents may be included to modify the properties of the polymerizable liquid used to coat the solid according to the process of this invention. The

applicable plasticizers are liquid materials which solvate, dilute or form gels with the solid material employed. Such plasticizers generally include the organic esters of dibasic organic acids, the esters of organic diols and triols and organic acids, polyoxyacids, the esters of polyalkylene glycols and organic acids, polyoxyalkylene diolalkylene oxides, liquid hydrocarbon oils, organic phosphates, phosphites and phosphonates, polyesters, fatty acid esters, as well as other materials. The plasticizers applicable to the present process are liquids at the particular temperature employed during the mixing in the inert carrier, and in general, are liquids at some temperature over the range of 0 to 150° C. Specific examples of applicable plasticizers (and their melting points in degrees Centigrade) include: methyl abietate, di-sobutyl adipate (-20), di-(2-ethylhexyl) adipate (-75), dihexoxyethyl adipate (-5), diethylene glycol dibenzoate (16-28), chlorinated coconut oil fatty acids (-20), glycerol monononanoate (-30), diethylene glycol dipropionate, diethylene glycol monolaurate (0-11), butyl oleate (-10), cresyl diphenyl phosphate (-40), dibutyl phthalate (-35), butyl octyl phthalate (-50), dibutoxyethyl phthalate, methyl ricinoleate (-30 pour pt.), dimethyl sebacate, di-isooctyl sebacate (-50), and dibutyl tartrate (20-22).

The process of this invention is useful in the preparation of inert or pigment loaded molding resins, encapsulated reactive materials, textured paint pigments, graded release materials in fine particulate form, coated pigments and other materials for use in systems where they are incompatible in unprotected form, particles coated with an intermediate bonding material to improve their bonding properties in subsequent use, and coated particles with other diverse uses.

When it is desired that the coating be completely impervious (as with encapsulated reactive materials) a high ratio of polymer to solid particles is employed. On the other hand when preparing graded release coatings, a low ratio of polymer to solids employed. The permeability of the coating is also dependent on the particular polymer employed.

The following examples, in which all parts and percentages are by weight unless otherwise stated, illustrate the process of this invention.

#### EXAMPLE I

Ammonium perchlorate having an average particle diameter of about 20 microns is dispersed in hexamethyldisiloxane so that the dispersion contains 10 weight percent ammonium perchlorate. A second dispersion in this same carrier is prepared from a hydroxyl terminated liquid polybutadiene having a molecular weight range of from 2000 to 8000, and a low mol weight (350 to 375) polyarylene-polyisocyanate polymer. The second dispersion contains 10 percent total dispersed material, 97 percent of which is the polybutadiene polymer. The two dispersions are blended in an agitated vessel having heating means and while agitation is maintained the mixture is heated at 180° F. for from 2 to 4 hours. After which time heating and agitation are discontinued and the polymeric-coated solid particles of ammonium perchlorate allowed to settle and the supernatant hexamethyldisiloxane is decanted. The resultant coated particles may be employed as a component of solid rocket propellant grains.

#### EXAMPLE II

Pigment grade copper phthalocyanine (80 parts) and 20 parts of a liquid copolymer of 90 mol percent ethyl acrylate, 5 mol percent glycidyl methacrylate, and 5 mole percent acrylic acid having an average molecular weight of from 1000 to 3000 are individually slowly added to an agitated vessel containing 500 parts of 1,1,2-trichloro-1,2,2-trifluoroethane. The vessel is maintained under agitation while the pigment and polymers are added and agitation is continued after the addition is complete. The agitated contents of the vessel are heated at 150° F. for about 3 hours and the resulting polymer coated particles of copper phthalocyanine may be subsequently employed after the removal of the carrier as an ingredient of paints or printing inks and have the advantage that the copper phthalocyanine will not bleed into the paint vehicle or ink carrier.

#### EXAMPLE III

Following the general procedure of Example II, 96 parts of finely ground urea and 4 parts of a liquid polymer prepared from 95 mole percent of butadiene and 5 mole percent allyl glycidyl ether having a molecular weight range of from 500 to 2000 are slowly added to 300 parts of trichloroethylene in the vessel. A trace amount of phosphoric acid is added as a curing catalyst for the polymer. After addition is complete, agitation is maintained while the temperature of the vessel is raised to 120° F.

for about 2 hours. After removal of the carrier, the resulting coated particles of urea may be employed as a slow release fertilizer. Since this small amount of the polymer does not form a completely impervious coating, the urea is still available to be dissolved by water, but the solution rate is much lower than uncoated urea particles.

5

**EXAMPLE IV**

A slurry of 100 parts, pigmented polyamide fibers having an approximate length of 1 mm., and 2000 parts of hexane is continuously blended with a dispersion of 100 part of a liquid, low molecular weight tetramethylene diamine-succinic acid polymer prepared from 1.1 moles of the diamine per mole of the acid and which has a molecular weight of from 500 to 2000. The polymer slurry also contains 3 percent of a low molecular weight polyarylene polyisocyanate resin having a molecular weight of about 550. The polymer slurry is made up from a total of 100 parts of polymer ingredients and approximately 2000 parts of hexane. The slurries are continuously mixed in apparatus having characteristics illustrated in Fig. 2 in such a fashion that the final mixture contains 85 percent pigmented polyamide fibers and 15 percent polymer. After passing through the mixing zone the continuous stream of individually coated fibers in the hexane carrier are conducted through a line reactor under high turbulence and maintained at a temperature of 100° F. in the reactor. The residence time in the reactor is approximately 5 minutes, at the end of which time the polymer coating is in a non-tacky condition. The partly polymerized coated particles in the carrier after removal from the line reactor are collected in an agitator vessel and maintained at 100° F. for one additional hour. At the end of hour, the polymer is completely cured, agitation is discontinued and the polymer coated polyamide fibers are separated from the hexane carrier. These coated fibers may be bonded to a cotton fabric base by means of an epoxy adhesive to give the effect of a colored synthetic felt.

5

10

15

20

25

30

35

40

45

50

55

60

**EXAMPLE V**

To an agitated and heated vessel containing 1000 parts of heptane is simultaneously added incremental portions of titanium dioxide, a liquid polymer of 95 mol percent methyl methacrylate and 5 mol percent acrylic acid having a molecular weight range of from 1000—3000, and a polymer of glycerine and epichlorohydrin having a molecular weight range of from 300 to 500. Approximately equal quantities of the polymer systems and titanium dioxide are employed and the resins are employed in a ratio such that the glycerine-epichlorohydrin resin constitutes 10 percent of the total polymerizable material. Agitation of the titanium dioxide and polymerizable materials continues until a total of 100 parts of each has been added to the agitable vessel. Agitation is continued after the addition is complete and the temperature of the slurry is maintained at 150° F. for about 5 hours. Upon cooling and removing the heptane from the system, there results individually coated particles of titanium dioxide which are employable as plastics molding powders containing an inert filler. Thus, the process of this invention provides loaded polymeric molding powders without the necessity of mixing the inert material and the polymers in a highly viscous form.

When the individual components employed in the process of this invention are not pre-dispersed in the carrier, but added to the carrier simultaneously or individually, the ratio of carrier to total carried material varies from 20:1 to 1:1. It is usually preferred, for ease of handling, that the ratio be maintained between 20:1 to 10:1.

**WHAT WE CLAIM IS:—**

1. A process for preparing a solid particulate material coated with a polymeric material, which process comprises mixing a solid particulate substance and a polymerizable liquid material under turbulent conditions and in the presence of an inert non-solvent liquid carrier so as to coat the solid with the polymerizable liquid and thereafter polymerizing the polymerizable liquid to a polymeric solid while maintaining turbulent conditions and thereby producing discrete solid particles coated with a solid polymeric material.
2. A process according to claim 1, wherein the said substance, polymerizable liquid and liquid carrier are brought together and mixed in a mixing zone.
3. A process according to claim 1, wherein the said substance and polymerizable liquid are first dispersed in separate mutually miscible liquid carriers (which may be the same or different liquids) to produce dispersions which are subsequently mixed.
4. A process according to claim 1, wherein there is initially dispersed in the liquid carrier one of the other components (namely the said substance and the polymerizable liquid) to produce a dispersion into which the other of the said other components is subsequently mixed.

5. A process according to claim 1, 2, 3, or 4, wherein the polymerizable liquid is a thermosetting organic material.

6. Any process according to claim 1, substantially as hereinbefore described including processes employing any of the specific solid particulate substances, polymerizable liquids and liquid carriers referred to and including processes given in Examples I to V.

7. A solid particulate material coated with a polymeric material prepared by a process according to any one of the preceding claims.

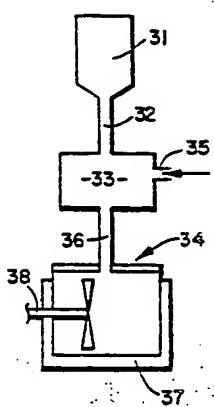
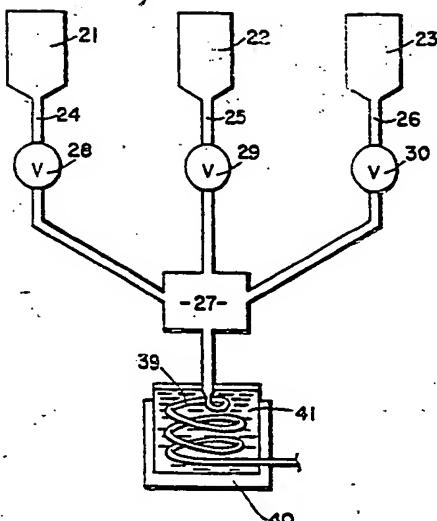
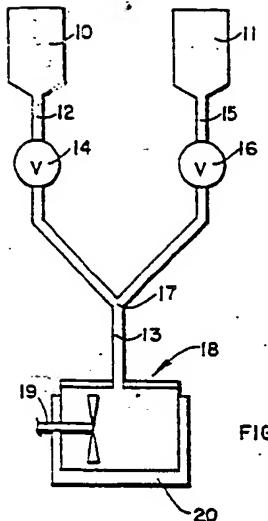
5

REDDIE & GROSE,  
Agents for the Applicants,  
6, Bream's Buildings, London, E.C.4.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press  
(Leamington) Ltd.—1966. Published by The Patent Office, 25 Southampton Buildings,  
London, W.C.2, from which copies may be obtained.

1025694 COMPLETE SPECIFICATION  
1 SHEET

This drawing is a reproduction of  
the Original on a reduced scale



**THIS PAGE BLANK (USPTO)**

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**

**THIS PAGE BLANK (USPTO)**